Photochemical Reaction of 1,4-Naphthoquinone with Olefins (Commemoration Issue Dedicated to Professor Sango Kunichika On the Occasion of his Retirement)

AUTHOR(S):

Maruyama, Kazuhiro; Otsuki, Tetsuo; Takuwa, Akio; Kako, Saburo

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Photochemical Reaction of 1,4-Naphthoquinone with Olefins

Kazuhiro MARUYAMA*, Tetsuo OTSUKI**, Akio TAKUWA** and Saburo KAKO**

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Photochemical reactions of 1,4-naphthoquinone with various types of olefins are examined. 1,4-Naphthoquinhydrone is produced in the reaction of 1,4-naphthoquinone with olefins having an abstractable allylic hydrogen atom. With the another types of olefins 1,4-naphthoquinone undergoes cycloaddition reaction to yield cyclobutene-type compounds (I) or cyclobutane-type compounds (II).

I. INTRODUCTION

Recently photochemical reactions have been the attractive field in the synthetic organic chemistry.[1] A variety of cyclobutane can easily be prepared by the application of photochemical reactions. Competitive formation of cyclobutanes and oxetans was reported when *p*-benzoquinones were irradiated in the presence of olefins.[2] Photochemical behaviors of 1,4-naphthoquinone have not been elucidated with the exceptions of its dimerization reaction,[3] and its reactions with indene, isocoumarin and benzofurane to give cyclobutane-type compounds.[4]

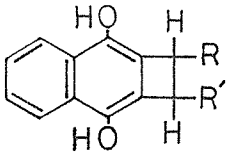
Olefins examined in this experiment are α-pinene, cyclopentene, cyclohexene, cyclooctene, acenaphthylene, indene and styrene.

II. RESULTS AND DISCUSSIONS

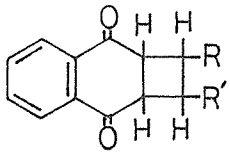
In the photochemical reaction of 1,4-naphthoquinone with α-pinene, cyclopentene and cyclohexene, 1,4-naphthoquinone is readily reduced to 1,4-naphthoquinhydrone. 1,4-Naphthoquinhydrone may be resulted from 1,4-naphthosemiquinone radical, which is produced through the hydrogen abstraction of photochemically excited 1,4-naphthoquinone. These processes might be analogous to those of photochemical reactions of *p*-benzoquinones with hydrogen donors.[5] Thus, α-pinene, cyclopentene and cyclohexene react with 1,4-naphthoquinone as hydrogen donors rather than olefins, since these olefins have the reactive hydrogen atom.

Another types of olefins, which seem to have no reactive hydrogen atom, add to 1,4-naphthoquinone to give cycloaddition compounds by irradiation. The photo-addition compounds are classified into two groups; cyclobutene-type compounds (I) and cyclobutane-type compounds (II). Cyclooctene and acenaphthylene give cyclobutene-type compounds in the photochemical reaction with 1,4-naphthoquinone (see (Ia) and (Ib))

* 丸山和博: Department of Chemistry, Faculty of Science, Kyoto University, Kyoto.
** 大槻哲夫, 宅和暁男, 加古三郎: Department of Chemistry, College of Liberal Arts and Science, Kyoto University, Kyoto.

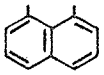


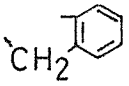
(I)



(II)

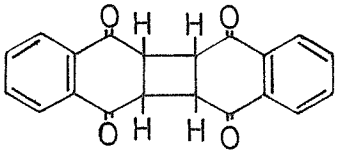
(Ia) R,R′: $-(CH_2)_6-$

(Ib) R,R′: 

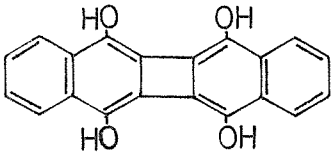
(IIa) R,R′: 

(IIb) R: -H, R′: 

and indene and styrene give cyclobutane-type compounds (see (IIa) and (IIb)). Factors differentiating between two types of photo-addition compounds, *i.e.* (I) and (II), remain to be clarified. However, cyclobutane-type compounds (II) might be the precursor at the earlier stage of the reaction since the photo-dimer (III) of 1,4-naphthoquinone as a primary reaction product is converted to 1,4,5,8-tetrahydroxy-2,3; 6,7-dibenzobiphenylene (IV) by the treatment with alkali.[3a] Concurrent formation of photo-addition com-



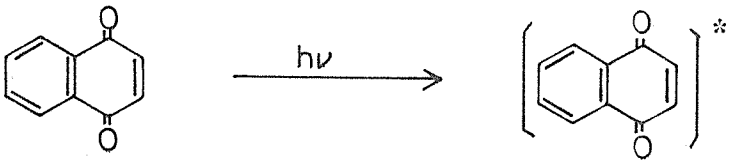
(III)

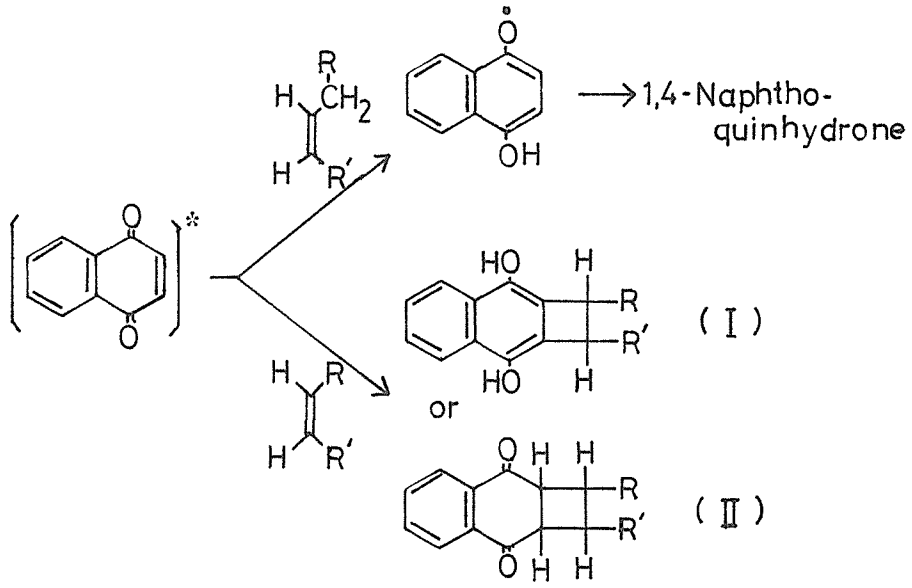


(IV)

pound (IIa) and 1,4-naphthoquinhydrone is observed in the reaction of 1,4-naphthoquinone with indene, presumably because indene has the reactive benzylic hydrogen atoms, which are comparable in their nature to allylic hydrogen atoms. Although cyclooctene is a higher analogue of cyclohexene, it gives a photo-addition compound of type (Ia). Molecular model reveals that cyclooctene has no active allylic hydrogen atoms owing to the deformation from the normal bond angles. Hence, cyclooctene reacts with 1,4-naphthoquinone to yield (Ia)-type photo-addition compound, but not 1,4-naphthoquinhydrone.

The principal course of the photochemical reaction is illustrated as follows;





Reaction Scheme

At the first stage of the reaction, 1,4-naphthoquinone is excited through the n-π^* excitation of the carbonyl group by irradiation. In the presence of hydrogen donors photochemically excited 1,4-naphthoquinone (characterized by "*" in Scheme) abstracts hydrogen atom to form 1,4-naphthosemiquinone radical. The lack of reactive hydrogen atoms should cause 1,4-naphthoquinone to add to olefinic double bonds. Considering these results, the abstraction of allylic hydrogen atoms by excited 1,4-naphthoquinone might proceed more easily than the other processes such as cycloaddition with olefins and dimerization of itself.[6]

III. EXPERIMENTAL

General procedures: 1,4-naphthoquinone was used after sublimation of commercially available guaranteed grade reagent (mp. 124.0–125.0°C). 10 mmol of 1, 4-naphthoquinone and 20 mmol of olefins were dissolved into 20 ml of benzene with an exception of cyclooctene. In the reaction of 1,4-naphthoquinone with cyclooctene carbon tetrachloride was used as solvent. The solution was poured into a usual glass tube, sealed and then irradiated for 20–40 hours by high pressure Hg lamp (400 W). The reaction vessel set apart by 5 cm long from the light source was immersed in water. The reaction products were isolated by column-chromatography on florisil and purified by recrystallization.

Physical properties of products;

(Ia); brownish white solid after washing with acetone and ether repeatedly. mp 303.0–303.5°C (decom.). IR; ν_{OH}: 3510 cm^{-1} (sharp), 3350 cm^{-1} (broad) (as KBr disk). NMR; τ: 1.50–2.70 (4H, aromatic-H, multiplet), τ: 5.40–6.35

(2H, methine-H, multiplet), 7.65–8.88 (12H, aliphatic-H, broad multiplet) (in the solution of CF_3 COOH-$CDCl_3$).

(Ib); yellowish white needles after recrystallization from chloroform. mp 296.0–298.0°C (decom.). IR; ν_{OH}: 3255 cm^{-1} (broad) (as KBr disk). NMR; τ: 2.20–2.58 (10H, aromatic-H, multiplet), τ: 5.92 (2H, methine-H, singlet) (in the solution of $CDCl_3$).

(IIa); white plates after recrystallization from benzene. mp 180.5–181.5°C IR; $\nu_{C=O}$: 1670 cm^{-1} (as KBr disk). NMR; τ: 1.65–2.30 (4H, aromatic-H due to 1,4-naphthoquinone rest, multiplet), τ: 2.65 (4H, aromatic-H due to indene rest, broad singlet), τ: 5.90–6.17, 6.58–6.95 (6H, methine-H and methylene-H, multiplet) (in the solution of $CDCl_3$).

(IIb); white plates after recrystallization from benzene and petroleum ether. mp 66.0–67.0°C. IR; $\nu_{C=O}$: 1670 cm^{-1} (as KBr disk). NMR; τ: 1.65–2.30 (4H, aromatic-H due to 1,4-naphthoquinone rest, multiplet), τ: 2.68 (5H, aromatic-H due to styrene rest, singlet), τ: 6.18–6.75, 7.12–7.35 (5H, methine-H and methylene-H, multiplet) (in the solution of $CDCl_3$).

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(6) This could be supported by the measurement of the reacting system using CIDNP methods.